

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/EP04/014894

International filing date: 23 December 2004 (23.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: EP
Number: 03078988.7
Filing date: 23 December 2003 (23.12.2003)

Date of receipt at the International Bureau: 18 January 2005 (18.01.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03078988.7

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:
Application no.: 03078988.7
Demande no:

Anmeldetag:
Date of filing: 23.12.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Corus Staal BV
P.O. Box 10000
1970 CA Ijmuiden
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Improved metal strip electroplating

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C25D/

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

Improved metal strip electroplating

The invention relates to electrolytic tinplating of packaging steel strip, using sacrificial anodes.

5 In the handbook "The Making, Shaping and Treating of Steel", 10th ed., p. 1146-1153, a description of a typical commercial tinplating process called FERROSTAN is given which is considered to be incorporated herein by reference.

As known, see also Figure 36-5 of said handbook, in the said known process the soluble anodes are to be replaced and the anode positions adjusted regularly,
10 which is labour intensive because of the weight of the anode bars of typically 50 kg, potentially hazardous in view of fumes, strong acids and high electrical currents and deteriorates the uniform tin coating thickness over the strip width.

When the anode bars are spent to an agreed minimum thickness, they are removed from the plating section and recycled in a remelting process for new cast
15 anodes.

Further, since optimal placement of the anodes is important for stable and uniform plating, the anode positions must be adjusted regularly.

It is thus an objective to minimize relatively unhealthy, heavy and uncomfortable work on parts of and above or near the plating unit.

20 Furthermore, it is an objective to provide a highly stable electroplating process that can be adequately controlled, minimizing disturbances caused by the supply, (lack of) adjustment and removal of anode parts.

At least some of these and other objectives and further advantages are achieved in a process according to aspects of the invention as claimed in claim 1,
25 claim 2 and/or claim 3.

The term "facing the strip" in this connection is intended to indicate that at least part of the anodic tin "is visible" from at least part of the strip.

In the process according to the invention the problem of having to adjust the anode positions to minimise tin edges when the strip path and/or the strip width
30 changes is avoided. Surprisingly, the necessary adjustments can be suitably made by controlled masking out part of the anode. In this context masking out is held to mean

2 / 10

positioning an object between anode and cathode so as to impede plating "in the shadow of the object" if the anode is seen as a light source.

In an embodiment of the invention wherein the anode substance, viz. tin is supplied in pellet form and fed to baskets, the tin bars are no longer there and so
5 there is no need to adjust them anymore. This embodiment is especially interesting for this electrolytic tinplating process because it eliminates the need to supply heavy anode bars. Instead anode substance is supplied in the form of more easily handled anode pellets. The invention also avoids removal of spent anode material since the pellets are completely consumed.

10 It is remarked that aspects of the improved electroplating process of the invention are claimed independently in claim 1 and in claim 2 and combined in claim 3.

Preferably the masking means have the features of claim 4. Surprisingly by simply masking edge portions of the anode it turns out to be possible to easily and
15 optimally control tinplating even at the edge portions of the strip.

The invention will now be elucidated using examples in the form of a description of aspects of the conventional process as a comparative example and aspects of the invention.

20 COMPARATIVE EXAMPLE: SACRIFICIAL ANODE SYSTEM

A typical soluble anode system is illustrated in Fig. 1. In Fig. 1 tin is supplied by tin anode 1 which has an anode gap 2 and an anode notch 3. Each of a series of tin anodes 1 is supported by an anode bridge 4 at a top portion near its anode notch 3 and at a bottom portion in anode box 5. Isolated plate 6 separates two tinning
25 sections in one plating cell. Electrical power is supplied to the strip via conductor roll 7. Near the bottom of the plating cell the strip is guided by sink roll 8. Also hold-down roll 9 is shown. Anode bridge 4 comprises an insulated parking space 10 for a fresh tin anode 1. The tin anodes 1 are connected to the anode bridge 4 via contact strip 14.

30 Three different procedures can be distinguished during operation of the soluble anode system.

3 / 10

Procedure 1 - Anode spacing

During tinplating the anodes have to be properly positioned to obtain a uniform tin coating thickness over the strip width. In Figure 2 an example is given of values of the tin coating thickness over the strip width in a situation in which the
5 anodes were not properly positioned.

To prevent the situation described above, the anodes have to be positioned as can be seen in Figure 3, which gives a top view of anode bridge.

Depending on the width of the strip 11, tin coating thickness and line speed, the optimal anode positions are given by parameters A-G. In one specific example
10 the optimal parameters are given for a line speed of 400 m min^{-1} , a strip width of 732 mm and a tin coating thickness of 2.8 g m^{-2} on each side of the strip.

- A = 95 mm (at height anode bridge) and 85 mm (at height anode box)
- B = 60 mm (at height anode bridge) and 50 mm (at height anode box)
- C = 13 mm
- 15 - D = 14 mm (anodes positioned at equidistance)
- E = 76 mm (fixed anode width); 8 anodes in total
- F = 50 mm
- G = 15 mm.

Using these settings a uniform tin coating thickness over the strip width can
20 be realised. Parameter C is of special importance as this position results in the well-known phenomenon "tin edge" also known as "dog-bone" effect.

Furthermore the anode is closer to the strip at the bottom to compensate for ohmic losses in the anode and strip, which would otherwise cause unwanted differences in current density over the height of the strip. Therefore parameter A and
25 B are smaller at the bottom of the anode than at the top.

In the soluble anode system, anode spacing is a regularly recurring operation after replacement of spent anodes (see procedure 2), after a change of strip width, and after a change to differential coating (see procedure 3). Anodes are manually spaced by placing an insulated hook into the anode gap.

30 Three important disadvantages of the soluble anode system can be identified due to the anode spacing.

4 / 10

- Variations of tin coating thickness over the strip width
 - Tin edges: outer anodes are too close to the strip edge (parameter C)
 - Anode streaks:
 - Non-equidistanced anodes (parameter D).
 - Anodes not evenly consumed over the length of the strip caused by improper anode positioning.
 - Labour intensive
 - Hazards
 - Exposure to electrolyte and fumes
 - Electrical current

Procedure 2 - Replacing spent anodes

The thickness of the worn anodes is regularly checked with a thickness gauge. When the anode thickness in the optimal anode arrangement previously described (see procedure 1) becomes less than 15 mm, the anode is detached from the anode bridge and placed on the nearest insulated parking space (see Fig. 4 showing how the anodes "move" along the anode bridge). On the other side a new anode is placed on the insulated parking space and transferred to the anode bridge. After each replacement, anodes need to be repositioned again (see procedure 1). In Fig. 4 a fresh tin anode is designated with N and a worn one with W.

During tinplating the anodes dissolve which results in a changing anode to strip distance. This causes a non-homogeneous tin coating thickness distribution over the strip width. In practice this is compensated by placing the anode bridge and the strip at a small angle (see procedure 1, parameters A and B).

The disadvantages of the soluble anode system due to anode replacement are mainly related to anode spacing (see procedure 1). An additional disadvantage is that the anodes are not constantly positioned according to the optimal anode arrangement during anode replacement. This causes variations in the tin coating thickness over the strip width.

Procedure 3 - Changing to another strip width or to differential coating

5 / 10

After changing strip width, parameter C in Figure 3 no longer has the optimal value. Furthermore after changing to differential coating, i.e. a lower coating weight on one side of the strip, tin edge build-up becomes more severe on the low coating weight side. In practice both situations are compensated by removing (or adding) and/or repositioning the anodes on the anode bridge.

In this connection reference is made to Fig. 5 indicating removing or adding anodes after changing to another strip width or to differential coatings.

If the strip width changes e.g. from 732 mm to 580 mm in the previously described optimal anode arrangement (see procedure 1) two anodes have to be detached from the anode bridge (see Figure 5). After removal of the anodes, the remaining anodes need to be repositioned again (see procedure 1).

If a differential coating is applied of $2.8 / 5.6 \text{ g m}^{-2}$ in the previously described optimal anode arrangement (see procedure 1) one anode has to be added on the anode bridge facing the high coating weight side of the strip. After adding, the anodes need to be repositioned again (see procedure 1). At more extreme coating weight differences the outermost anodes also have to be shifted more inwards (parameter C in Figure 3) with respect to the strip edge.

DISADVANTAGES PRIOR ART AND ADVANTAGES INVENTION

The disadvantages of the soluble anode system due to changing to another strip width or to differential coating are mainly related to anode spacing (see procedure 1). An additional disadvantage is that the anodes are not positioned according to the optimal anode arrangement (see procedure 1) during removal or adding of anodes. This causes variations in the tin coating thickness over the strip width.

To overcome the disadvantages of soluble anodes (SA) mentioned in the comparative example, dimension stable anodes (DSA) are sometimes used. This system is less labour intensive and results in less variations of tin coating thickness over the strip width. The main disadvantage of DSA is that an external dissolution reactor is required to replenish tin to the electrolyte.

According to the invention the advantages of an SA and a DSA system are

6 / 10

now combined into a system which is totally new for high speed strip electroplating, the new system hereinafter referred to as a DSSA (dimension stable soluble anode) system.

According to the method of the invention more uniform tin coatings can be applied, even where it is less labour intensive, involves less hazards and is lower in costs. The tin stock can be lower and compared to the DSA system no separate dissolution reactor is needed. Also less personnel is needed for anode handling. Also, by using as the anode tin in the form of pellets held in an anode basket according to the invention, the cell voltage can be lowered. Probably this is due to the increase of anodic surface. It will be clear that thus also opens up routes to increased production speeds and thus potentially higher yield for the electroplating production line in question.

The invention will now be described in more detail by describing an example according to the invention.

EXAMPLE ACCORDING TO THE INVENTION

In the example according to the invention the plating installation parts and the process fluids and parameters were conventional except where mentioned.

According to an aspect of the invention instead of individual tin bars, reference being made to Figures 1 and 6, anodebaskets 12 were mounted on the anode bar 4 via contact strip 14. The contact strips 14, made of copper in the experiments according to this example, may be coated on their surface contacting the anodebasket 12 with a noble metal like Au or Pt. In the embodiment of the invention the contact strips 14 were coated with Pt, which worked well.

The anode baskets 12 in Fig. 6 were filled with tin pellets (2-20 mm preferably between 5-9 mm in diameter). In order to replenish anodic substance, tin pellets are supplied regularly, which can be done while the plating line is fully operational. The anode baskets 12, in the experiments according to this example made of titanium, are designed and positioned in such a way that the anode is closer to the strip at the bottom to compensate for ohmic losses in the anode and strip, which would otherwise cause unwanted differences in current density over the height

7 / 10

of the strip. For part of the production according to this example, the anode basket was covered with an anode bag to prevent small tin fines entering the electrolyte. Under normal operating conditions the anode bags may need replacement 1-2 times a year. On the other hand, it turned out that for another part of the production according to this example where no anode bag was used, this did not pose a problem of small tin fines entering the electrolyte. Apparently anode bags may not be necessary.

By providing the DSSA system with an edge mask 13, see Fig. 7, even the build-up of tin (dogbone effect) can be reduced. The construction of these edge masks and the system to move them are designed in such a way that they can be operated from a safe distance from the plating line excluding labour intensive and possibly dangerous work.

In a cathode/anode geometry where the strip width is 1020 mm and the anode width exactly overlaps the strip at also 1020 mm, when the strip width is subsequently changed from 1020 to 940 mm, the relative current density i/i_{avg} and therefore the amount of tin build-up at the edge of the strip reaches an unacceptable level, see upper curve in Fig. 8.

In Fig. 8 the horizontal axis shows D ES representing the distance in mm from the edge of the strip, the lower curve shows the relation i/i_{avg} versus D ES for a strip and anode width of 1020 mm, and the upper curve shows i/i_{avg} after the strip width has changed to 940 leaving the anode configuration configured for a strip width of 1020 mm.

To overcome this problem a shutter is placed as a mask in front of the anode basket. In Fig. 9 a schematic representation of this situation is given. In Fig. 9 the vertical axis (the Y-axis) represents a plane through the centre of the strip perpendicular to the surface of the strip. Y=0 represents a cross section of the face of the strip, and Y=50 represents a cross section of the face of the anode and the values on the Y-axis represent the distance from the cathode abbreviated as D AC. The horizontal axis (the X-axis) represents the distance from the centre of the strip, D CS. The grey area at X = (450;700) and Y=(10;15) represents a cross section of the shutter indicated by M.

8 / 10

If in Fig. 9 the placement of the shutter is varied from $X = 470$ mm (corresponding to 0 mm overlap with a strip having a width of 940 mm) to 440, 425 and 410 mm (corresponding to an overlap with the strip of 30, 45 and 60 mm respectively) the current density at the edge of the strip is reduced, see Fig. 10. In
5 Fig. 10 the upper curve corresponds to an overlap of 0 mm, the next lower curve to 30 mm, the next lower curve to 45 mm and the lower curve to 60 mm.

In practice, an optimum tin layer thickness distribution may be found at an overlap of mask and anode of about 45 mm.

It will be clear that the invention involves a great leap forward whereby the
10 features and operation of existing electroplating lines can be greatly improved by providing a method that can be easily controlled, is less labour intensive, eliminates risks and reduces waste (regeneration) flows.

9 / 10

CLAIMS

1. Process for high speed metal strip electroplating wherein the strip is plated by anodically dissolving tin anodes facing the strip into an electroplating solution, and depositing said anodically dissolved tin on at least part of the strip acting as cathode, wherein part of the anode is masked out using adjustable masking means that are adjusted dependent on at least one of strip width and/or tin coating thickness distribution.
2. Process for high speed metal strip electroplating wherein the strip is plated by anodically dissolving tin anodes facing the strip into an electroplating solution, and depositing said anodically dissolved tin on at least part of the strip acting as cathode, wherein tin is supplied to the electroplating solution in the form of pellets held in an anode basket.
3. Process for high speed metal strip electroplating wherein the strip is plated by anodically dissolving tin anodes facing the strip into an electroplating solution, and depositing said anodically dissolved tin on at least part of the strip acting as cathode, wherein the metal is supplied to the electroplating solution in the form of pellets held in an anode basket and wherein part of the anode is masked out using adjustable masking means that are controlled and guided dependent on strip width and/or tin coating thickness distribution.
4. Process according to claim 1 or 3, characterised in that the masking means comprise a shutter.
5. Process according to claim 4, characterised in that the shutter is in the form of a blind.
6. Process according to any one of claims 2 – 5, characterised in that the tin pellets are electrically contacted via a current collector made of a material with a low electrical resistance allowing for good electrical contact with the tin pellets and

10 / 10

being chemically inert in the electrolyte.

7. Process according to claim 6, characterised in that the anode basket is so designed that it is the current collector.
8. Process according to any one of claims 2 – 6, characterised in that an automated
5 supply system is provided to add tin pellets to the anode basket.

1/10

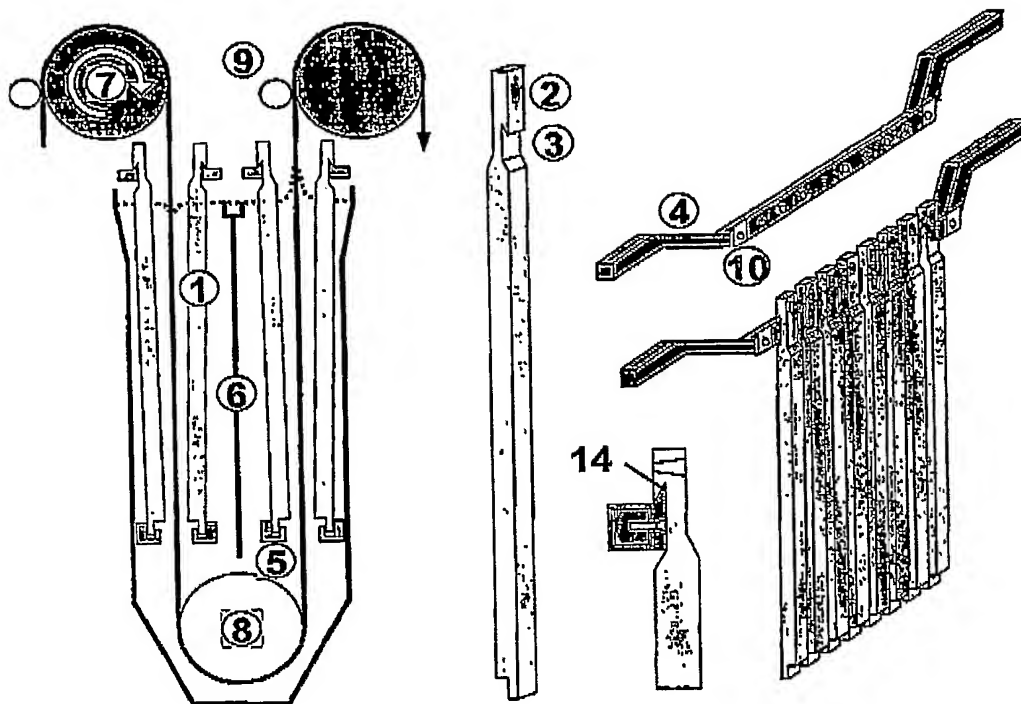


Fig. 1

2 / 10

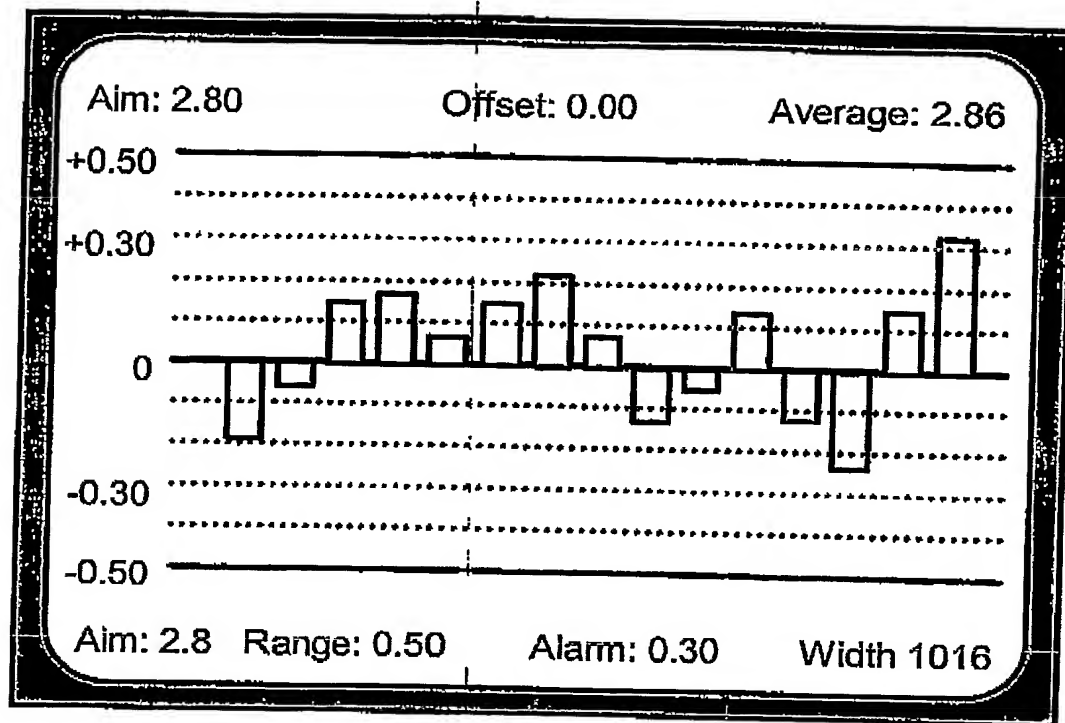


Fig. 2

3 / 10

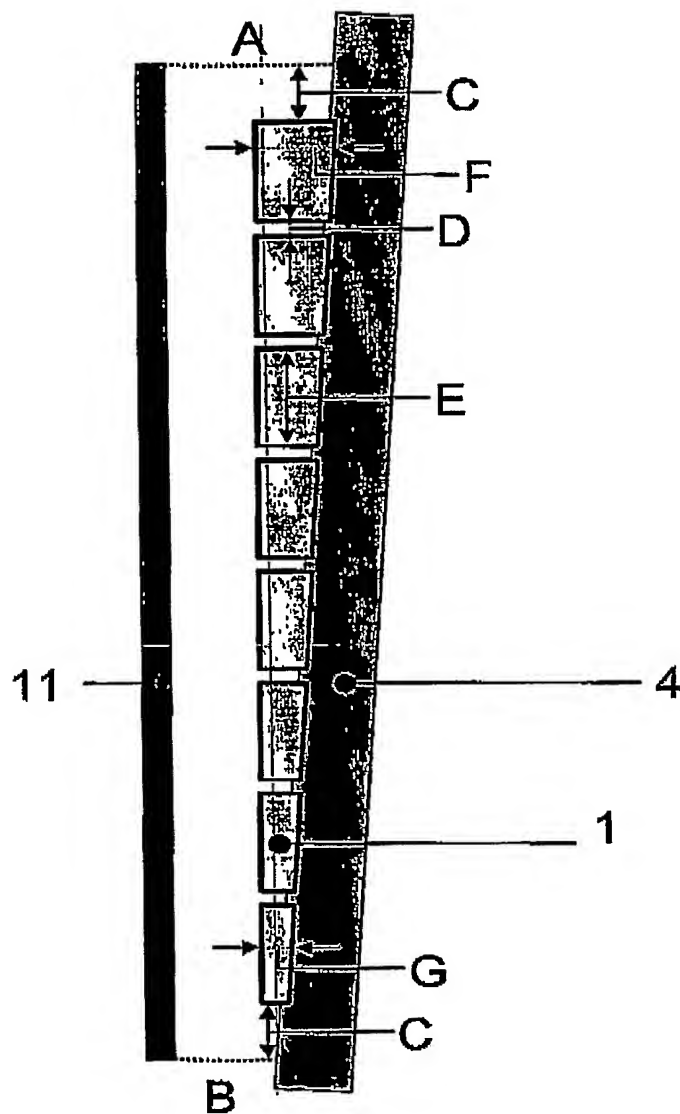


Fig. 3

4 / 10

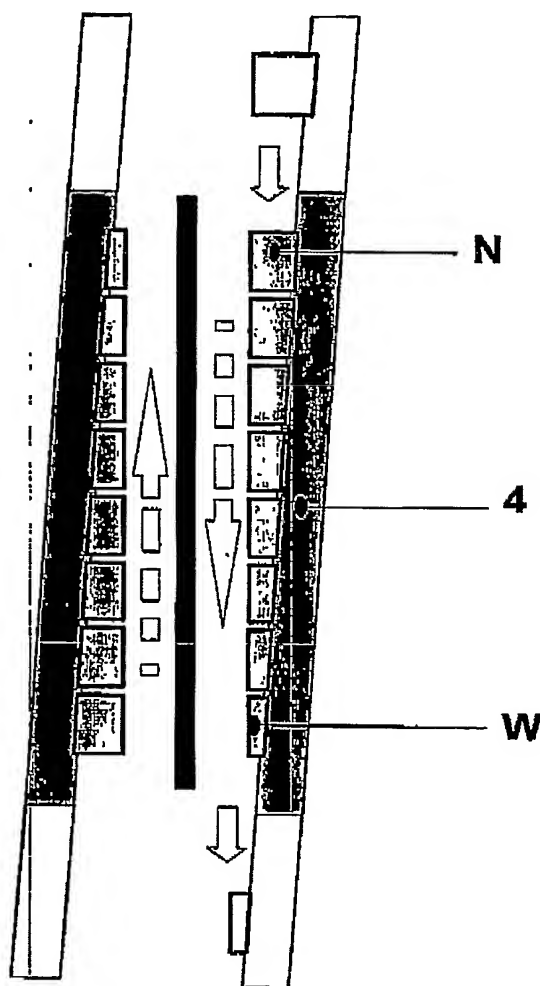
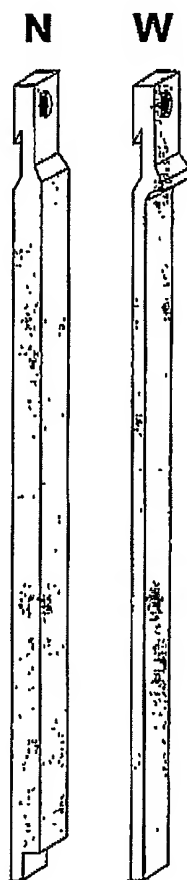


Fig. 4

5 / 10

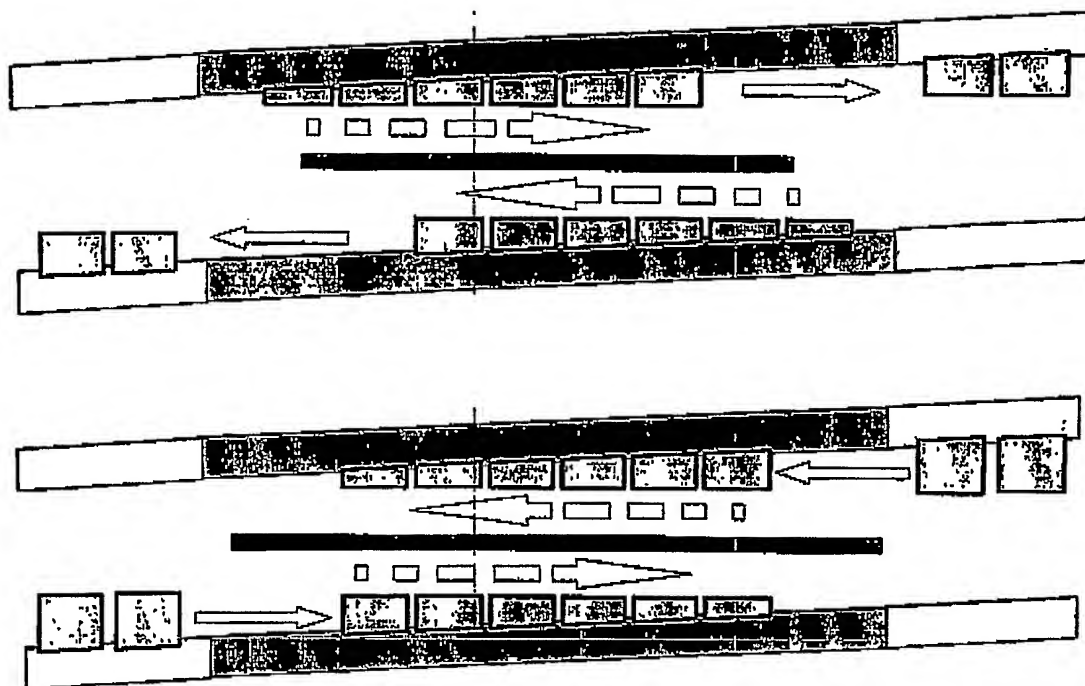


Fig. 5

6/10

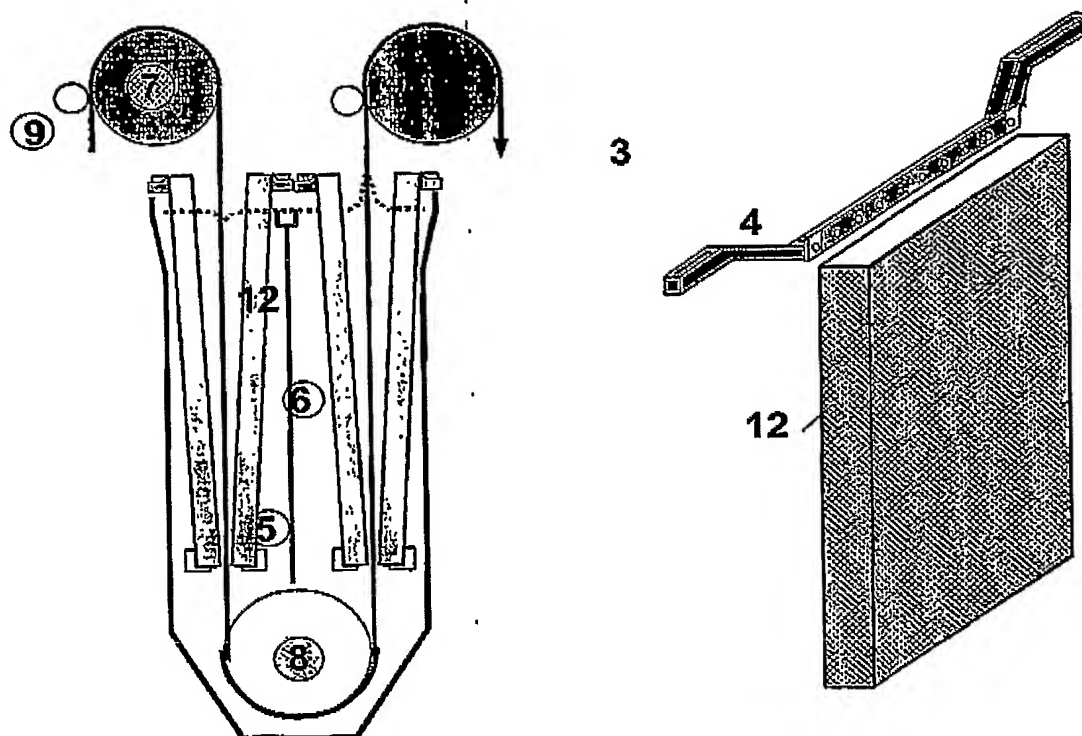


Fig. 6

7/10

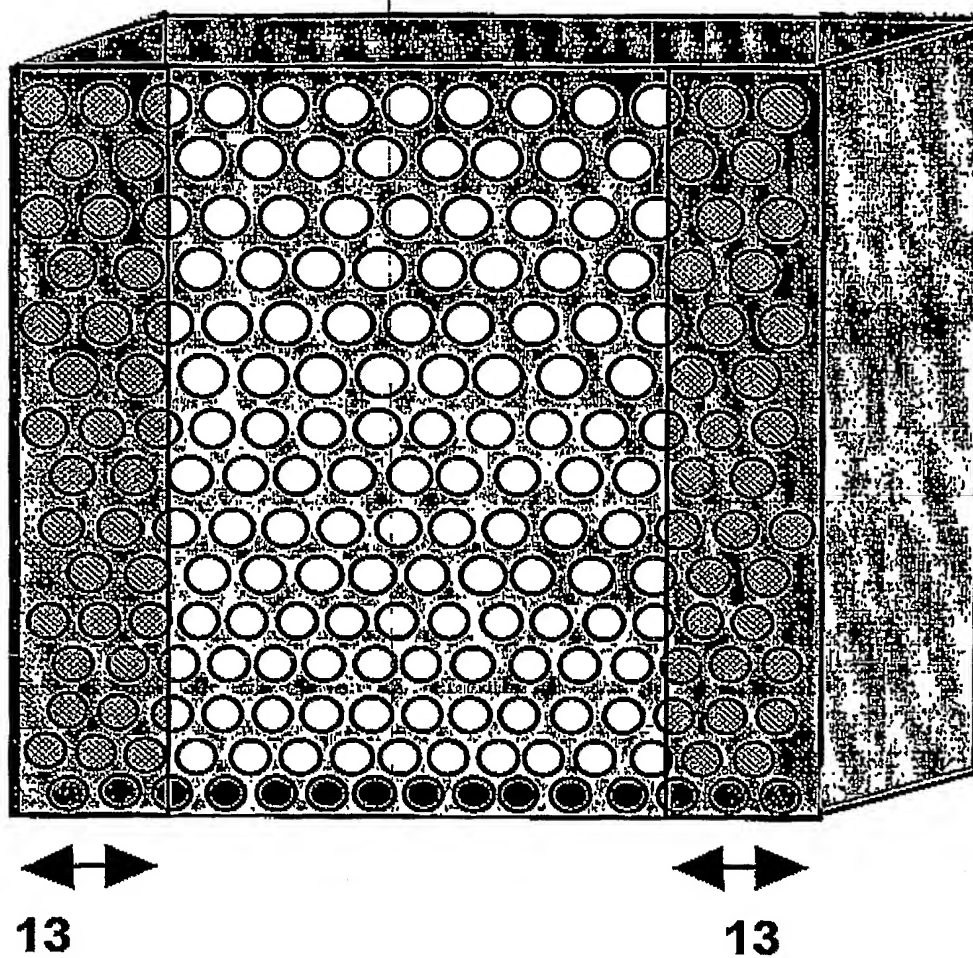


Fig. 7

8 / 10

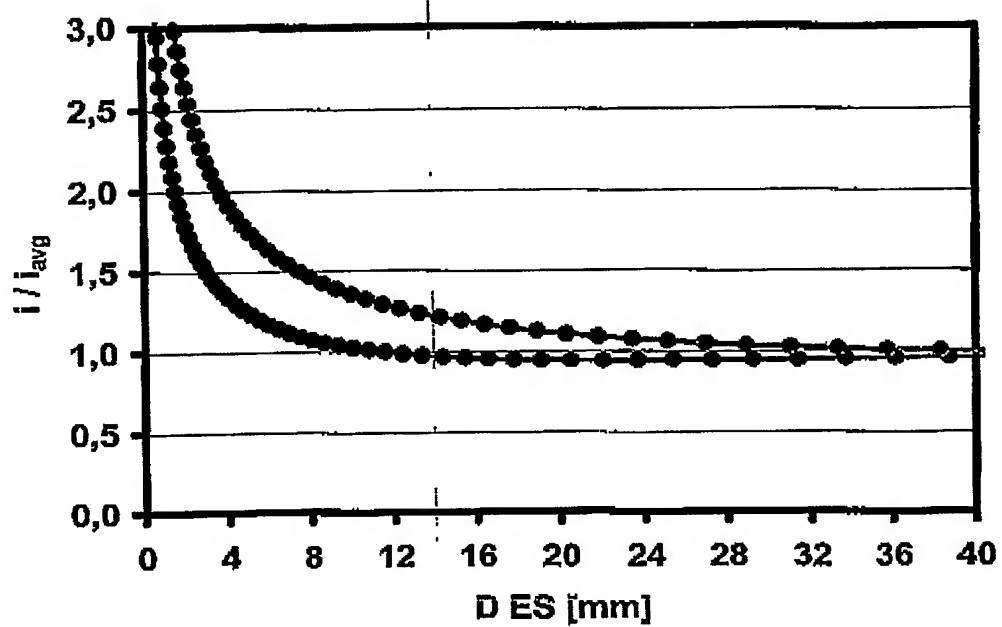


Fig. 8

9/10

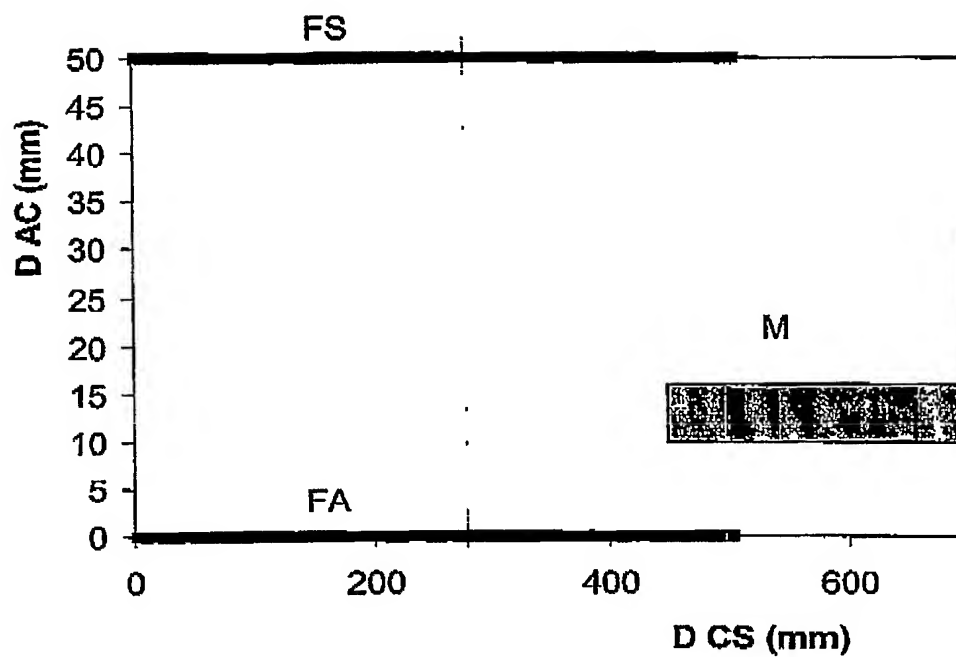


Fig. 9

10 / 10

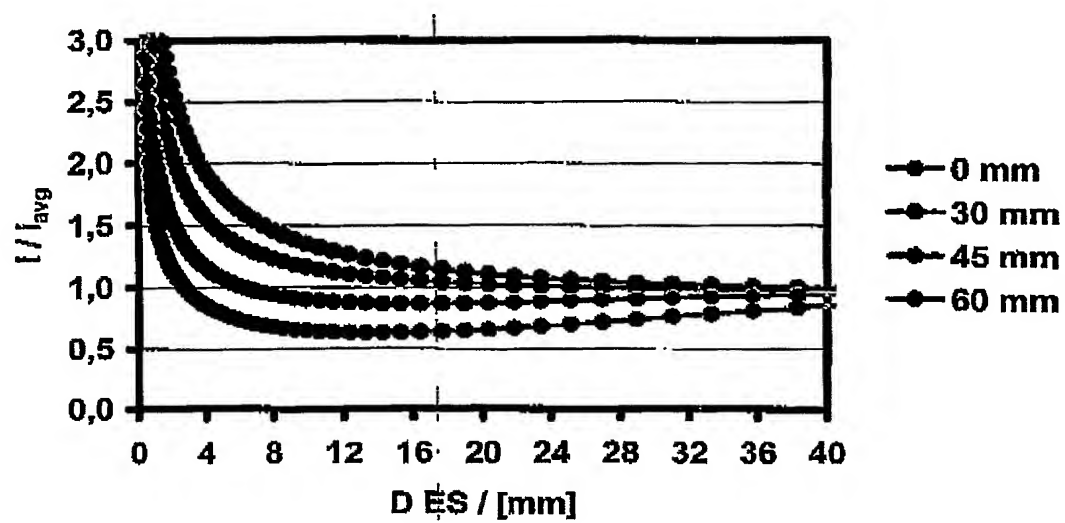


Fig. 10